CORROSION CHARACTERISTICS OF SOME MAGNESIUM-ZINC-CALCIUM ALLOYS[1]

G. C. KUCZYNSKI[2] AND F. SCHONFELD[3]

ABSTRACT

The resistance to corrosion of 45 cast Mg-Zn and Mg-Zn-Ca alloys was investigated by fourteen day exposure to an alternate immersion test. The data indicate that the corrosion rate increased with increasing zinc content in the range studied which included from 0 to 5.5% zinc. The corrosion rate was sharply reduced by addition of calcium in concentrations from 0.10 to 0.55%.

INTRODUCTION

It is commonly accepted that the corrosion of pure magnesium in salt solutions is an electrochemical process. The hydrogen gas is evolved on the cathodic parts of the metal (1) and on the anodic areas magnesium ions (Mg^{++}) pass into solution and in subsequent reaction with hydroxyl ions form magnesium hydroxide. With time the corrosion reaches a steady state whose rate is constant and lower than the initial rate. This is due to the formation of a hydroxide film, which eventually grows over cathodic areas and causes the polarization of the corrosion cells. The existence of such a film was established by electron diffraction studies (2). This film, however, is penetrable by chloride ions (Cl^-) and insufficiently adherent to prevent peeling off with the result that corrosion proceeds indefinitely although at a lower rate.

The binary alloys of magnesium corrode in general faster in salt solution than does pure magnesium (3) (4) (6). The only exceptions are manganese and low calcium content alloys as reported by Boyer (7) and Beck (9), which exhibit lower corrosion rates than pure magnesium if manganese or calcium are present in suitable concentrations. For the present investigation a series of magnesium-zinc alloys were chosen. Zinc improves greatly the mechanical properties of magnesium. Hardness of its alloys increases rapidly with zinc content as can be seen in Fig. 3. Endo and Morioka (4) reported supposedly beneficial influence of zinc upon the corrosion resistance of magnesium. Endo's findings however are contradictory to the results of Hanawalt's experiments (6). The experimental data discussed later in this paper agree with those obtained by the latter. The addition of calcium to magnesium-zinc alloys, as is shown in this paper, has a great effect upon the corrosion rate offsetting almost completely the deleterious effect of zinc.

MATERIALS AND METHOD

Magnesium-zinc and magnesium-zinc-calcium alloys were prepared from magnesium metal supplied by Permanente Metals Co., in California.

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[2] Present address: Sylvania Electric Products Inc., Bayside, L. I., N. Y.
[3] Present address: P.O. Box 1663, Los Alamos, New Mexico.

The magnesium contained the following impurities: silicon 0.005, lead 0.005, iron 0.001, copper 0.0005, manganese 0.0001 and calcium 0.05%. The principal impurities in the zinc metal used for alloying were iron, nickel, and copper each of which was below 0.001%. The zinc-calcium master alloys containing 5.30, 14.80, 34.35, 44.20 and 60.80% of calcium were made by electrolysis of molten calcium chloride on a cathode of molten zinc. From these master alloys and pure magnesium, the alloys containing up to 5.5% zinc and 0.7% calcium were prepared by melting pure magnesium and other alloys in a graphite crucible under fluoride flux.

After thorough mixing the alloys were chill-cast into graphite molds and then chemically analyzed. Calcium was determined gravimetrically as oxalate. The calcium content was always found to be lower than that calculated from the composition of the master alloys. This loss was attributed to oxidation. The ingots were cut into plates $1\frac{1}{2}$ inches (3.75 cm.) long, $\frac{3}{4}$ inch (1.87 cm.) wide, and $\frac{1}{8}$ inch (0.31 cm.) thick. The surfaces were ground and the dimensions measured with a micrometer. The weighed specimens were then hung on glass hooks in the corrosion chamber. The standard corrosion test, namely an alternate immersion in 3% sodium chloride solution, was adopted. The cycle was one half minute in air, followed by two minutes in the solution. The temperature in the chamber was maintained at 95°F. Each set of five specimens cut from one alloy was dipped in a separate beaker, the solution being changed every day. After fourteen days the specimens were removed from the chamber, washed in water and boiled in 20% chromium trioxide plus 1% silver chromate solution for two minutes in order to remove the products of corrosion (5). After drying they were weighed again. The difference in weight, ΔW, divided by time t (14 days), and total surface of the specimen, S, obtained from the linear dimensions is the average rate C of corrosion sought.

$$C = \frac{\Delta W}{St}\left(\frac{\text{gram}}{\text{cm}^2 \times \text{day}}\right)$$

EXPERIMENTAL RESULTS

Forty-five magnesium-zinc and magnesium-zinc-calcium alloys containing up to 5.50 weight per cent zinc and from 0 to 0.70 weight per cent calcium were investigated. The results are represented in Fig. 1 and 2. The upper curve of Fig. 1 represents the change of the corrosion rate C with zinc content in pure magnesium.

Endo and Morioka (4) determined corrosion rates for some magnesium-zinc alloys in aqueous sodium chloride solution but under less severe conditions. Their specimens were immersed continuously in weak 0.1 N sodium chloride solution. They however found that the corrosion rate decreases slightly with increasing zinc content. They were using magnesium metal with a relatively high iron content (0.019%) while J. D. Hanawalt (6) found that any iron content above the tolerance limit of 0.016% increases the corrosion rate enormously. Hanawalt observed further that the addition of zinc to magnesium-iron alloys exceeding this tolerance limit lowers the corrosion rate of the alloy but does not change

the tolerance limit itself. This is due to the formation of cathodes composed of zinc-iron alloy which are less electropositive than iron itself. Using very pure magnesium metal, Hanawalt (6) observed the appreciable increase of corrosion rate after 2% zinc was exceeded. These results are somewhat lower than those obtained by the authors. Also Murakami (3)

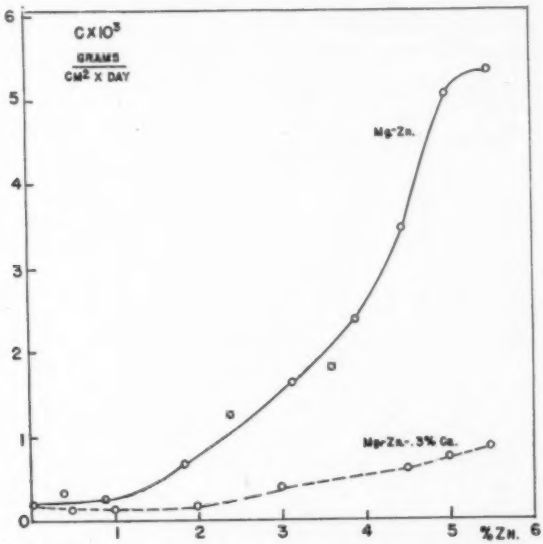

FIG. 1. Corrosion rate C as a function of Zn content

TABLE I

Alloy	C $\frac{\text{gram}}{\text{cm}^2 \times \text{day}}$
Mg	2.4×10^{-4}
Mg + .06% Ca	1.42×10^{-4}
Mg + .13% Ca	1.87×10^{-4}

investigated corrosion of some magnesium zinc alloys made of pure magnesium and found a steady increase in the corrosion rate with increasing zinc content.

Only two alloys of magnesium with calcium were made, one containing 0.06% calcium, the other 0.13%; both exhibited lower corrosion rate than pure magnesium, as shown in Table I.

In fig. 2 the corrosion rates of several calcium-bearing magnesium-zinc alloys are plotted against calcium content, each curve representing a

definite magnesium to zinc ratio with varying calcium content. It is noted that C is rapidly reduced as the calcium content is increased from zero to about 0.1%, is approximately constant for a given magnesium to zinc ratio up to about 0.5% calcium, then increases as the calcium content is increased. It is also noted that, regardless of the calcium content, the corrosion rate C increases with zinc content. Local attack in the form of pits was observed. The depth and diameter of these pits increased as the zinc content was increased. Some alloys containing more than 6% zinc were practically disintegrated after an exposure of two weeks.

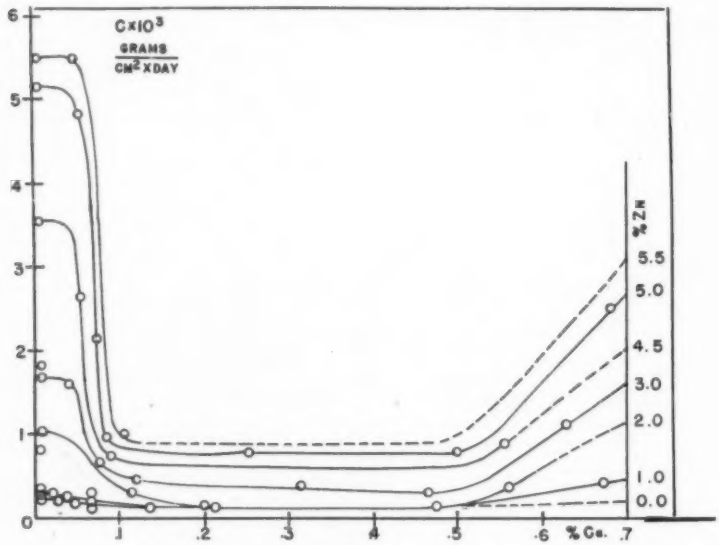

FIG. 2. Corrosion rate C as a function of Ca content

DISCUSSION OF THE RESULTS

The lowering of the corrosion rate of magnesium-zinc alloys with small amounts of calcium is best illustrated by comparing the two curves in Fig. 1. The upper curve represents the corrosion rate as a function of zinc content of the binary magnesium-zinc alloy series and the lower one shows the variation of corrosion rate for the same series of magnesium-zinc alloys with the addition of 0.3% calcium. In the case of 5.5% zinc in magnesium, the addition of calcium lowers the corrosion rate by more than 600%. The corrosion rate of pure magnesium is only slightly lowered by additions of calcium as seen in Fig. 2, and Table I.

The following mechanism is suggested as a tentative explanation of the above experimental data. The possibility of galvanic corrosion may be ignored for low calcium and zinc concentration since such alloys are solid solutions. All alloys were cooled so rapidly from the melting point that zinc was retained in solid solution even at concentrations as high as 5.0%.

Metallographic sampling and the smooth hardness curve (Fig. 3) taken on the binary magnesium-zinc alloys seem to prove that these alloys can be regarded as solid solutions. The solubility of calcium in magnesium is 0.83% at 300°C. as determined by W. Bulian (8), but according to Beck (9) at lower concentrations (0.4%) some Mg_2Ca may precipitate out. It is quite probable that magnesium-zinc-calcium alloys with more than 0.4 or 0.5% calcium contain some $Mg_5Ca_2Zn_5$ (10).

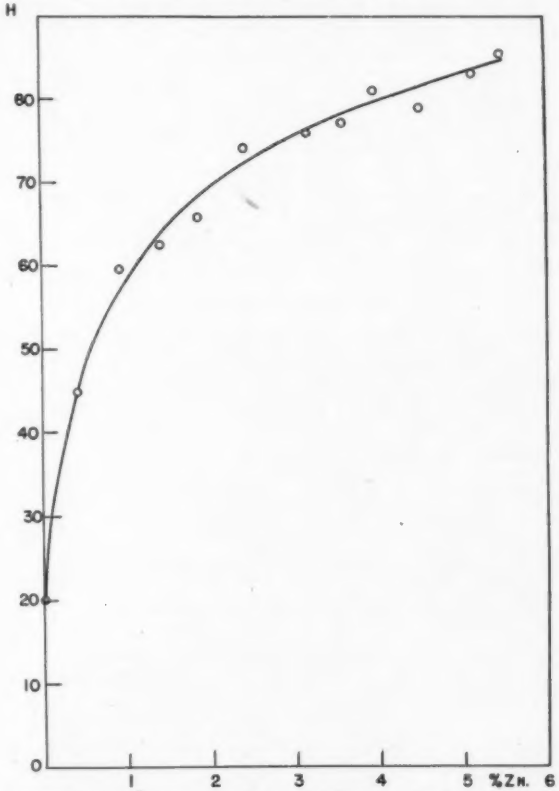

FIG. 3. Rockwell hardness (H scale) as a function of Zn content

As stated in the introduction, the formation of magnesium hydroxide and its deposition on the surface of the metal slows down the rate of corrosion appreciably but does not eliminate it. If zinc is alloyed with magnesium, zinc hydroxide forms and, since its solubility product constant (1.8×10^{-14}) is lower than that of magnesium hydroxide (1.2×10^{-11}), zinc hydroxide precipitates out taking hydroxyl ions from the solution while magnesium continues to dissolve. The higher the zinc concentra-

tion, the less protective is magnesium hydroxide due to the presence of less adhesive zinc hydroxide or zinc carbonate; consequently, corrosion proceeds with increasing rate.

If calcium is added in suitable concentration to magnesium-zinc alloy, it will go into solution producing additional hydroxyl ions. Because the calcium hydroxide solubility product constant (7.9×10^{-6}) is much higher than that of magnesium hydroxide, it will lower appreciably solubility of the latter by the common ion effect, forcing magnesium hydroxide out of solution and its consequent deposition on the surface of the alloy thereby decreasing its corrosion rate. It has to be noted however that some zinc hydroxide is deposited also rendering the film less adhesive and resulting in higher corrosion rates than in the absence of zinc (compare Fig. 2). The alloys with the concentration of calcium higher than 0.5% will probably contain some precipitate of $Mg_5Ca_2Zn_5$ which will furnish tiny cathodes accelerating corrosion. This is observed on the curves of Fig. 2 which rise when the concentration of 0.5% calcium is exceeded. In this stage the corrosion is of galvanic character. The above suggested explanation is by no means completely proven but at present seems to be plausible and adequate.

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ELECTRODEPOSITION OF LEAD FROM THE ETHYLBENZENESULFONATE BATH[1]

FRANK C. MATHERS
Indiana University, Bloomington, Ind.
AND
JOHN F. SUTTLE
University of New Mexico, Albuquerque, New Mexico

ABSTRACT

A cheaper or more satisfactory lead plating and refining bath than the usual ones with fluoborate or fluosilicate would be desirable. Lead salts of many organic sulfonates are soluble but, so far, satisfactory lead deposits have not been obtained.

Ethylbenzene is very easily sulfonated and lead ethylbenzenesulfonate is readily soluble. The usual addition agents, glue and goulac, did not prevent the rapid formation of trees from the cathodes, especially on the corners and edges. Many different addition agents were tried, but none gave as good deposits as could be obtained from corresponding lead fluosilicate baths. The best results were with β-naphthol and glue, or goulac, or both.

Literature. Little has been published on electrolysis of lead salts of organic sulfonates; Betts (1) reported poor results with lead benzenesulfonate, which is not very soluble, and benzenesulfonic acid was difficult to prepare and the deposits were loosely crystalline.

SULFONATION OF ETHYLBENZENE AND PREPARATION OF THE BATHS

Ethylbenzene, now available in commercial quantities for use in artificial rubber production, is easily sulfonated by merely shaking at the boiling point with an equal volume of concentrated sulfuric acid (sp. gr. 1.83). The reaction is complete when the two liquids become miscible. After cooling and adding a little water, the ethylbenzenesulfonic acid crystallizes (2). The acid is mostly the para-form. The aqueous solution of this crude sulfonic acid, containing 2.01 moles of the acid, was neutralized with lead carbonate and the insoluble lead sulfate was removed by filtration. The final plating bath, containing 50 g./L of lead and 60 g./L of free sulfonic acid, was made by adding the calculated quantity of sulfuric acid to the lead ethylbenzenesulfonate.

The lead anodes were cast in graphite molds. The cathodes were sheet iron one inch (2.5 cm.) square. The current was 25 amp./ ft.^{2} (2.7 amp./ dm.^{2}). The volume of each bath was 100 ml. in a 150 ml. beaker. The baths were operated at room temperature and were agitated just enough to prevent stratification. They were in continuous operation anywhere from one day to twenty-five days depending on the condition of the deposit.

Experimental Results. The quantity of addition agent or agents used was gradually increased in each bath from a small quantity (usually 1

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g./L) to saturation, or until it was evident that a solid, noncrystalline deposit could not be obtained. Without addition agents, projecting trees or crystals quickly produced short circuits. Table I gives the results with a variety of addition agents.

TABLE I.—*Comparison of addition agents*

No.	Other agents	Glue	Goulac	Glue and goulac together	Type of deposit
1	None	x			Very treelike around edges. Coarse on face
2	None		x		Same as 1
3	None			x	Slight improvement over 1 and 2
4	o-Cresol		x		Treelike on corners. Not very crystalline. Adherent
5	Resorcinol		x		Spongy deposit non-adherent
6	Phenol		x		Very crystalline and treelike. Adherent
7	β-Naphthol		x		Good deposit, knotty on corners but no trees. Adherent
8	β-Naphthol	x			Similar to 7, lighter in color than 7. Adherent
9	m-Cresol	x			Treelike on corners, very crystalline, light grey. Adherent
10	isoeugenol		x		Treelike on corners, crystalline, adherent
11	isoeugenol			x	Treelike on corners, crystalline, adherent
12	Dowicide		x		Very poor, trees all over face of cathode. Adherent
13	p-Amino phenol		x		Slightly treelike, not very crystalline. Adherent
14	o-Cresol diphenyl sulfone			x	Not much different from 4
15	Resorcinol diphenyl sulfone		x		Similar to 5
16	m-Cresol diphenyl sulfone			x	Treelike, coarsely crystalline. Adherent
17	β-Naphthol diphenyl sulfone	x			Similar to 7 and 8
18	β-Naphthol			x	Similar to 7 and 8
19	Isoeugenol diphenyl sulfone		x		Similar to 10 and 11
20	1-Amino-anthraquinone	x			Very adherent
21	1-Amino-2-naphthol,-4-sulfonic acid	x			Knotty on corners not very crystalline
22	Vanillyl alcohol	x			Not adherent
23	Urea	x			Treelike, not very crystalline
					Good deposit, knotty on corners. Non-crystalline, adherent
					Very treelike, crystalline, non-adherent, very poor deposit

CONCLUSION

The glue or goulac or both were not effective without some other material.

Some definite optimum concentrations of the combinations of the addition agents in g./L for obtaining the smoothest firm deposits are: glue, 2, and vanillyl alcohol, 2; or goulac 6, and β-naphthol 6; or β-naphthol 6, and glue, 5. p-Aminophenol and 1-aminoanthraquinone with glue-goulac gave fair deposits.

This bath is not recommended for plating because the deposits are not as good as from baths now in use.

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